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(54) A method of forming poly-(3-substituted) thiophenes

(57) A method of forming a regioregular polythiophene from a polymerization reaction is described. The method proceeds by combining a soluble thiophene

having at least two leaving groups with an organomagnesium reagent to form a regiochemical isomer intermediate, and adding thereto an effective amount of Ni(II) catalyst to initiate the polymerization reaction.

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Description**BACKGROUND OF THE INVENTION****5 Field of the Invention**

[0001] The present invention is directed, generally, to a method of forming poly-(3-substituted) thiophenes and, more particularly, to a method of forming head-to-tail coupled regioregular poly-(3-substituted) thiophenes.

10 Description of the Invention Background

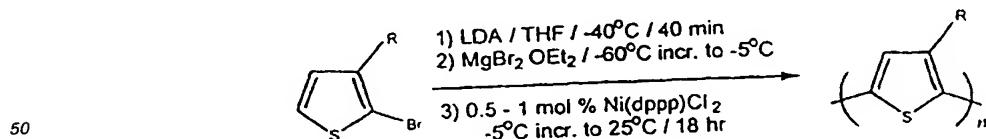
[0002] Poly-(3-substituted) thiophenes (PTs) represent a class of polymer that are highly processable and exhibit relatively high environmental stability, thermal stability, and electrical conductivity. As a result, these materials have been found to be promising candidates for numerous applications, ranging from electronic and optical devices, such as field-effect transistors, sensors, light-emitting diodes (LEDs), rechargeable batteries, smart cards, and non-linear optical materials, to medical applications, such as artificial muscles. The discovery of additional applications and new technologies is subject, in large part, to molecular designers ability to control the structure, properties, and function of PTs chemical synthesis. Those in the art have come to recognize that structure plays an important, if not critical role, in determining the physical properties of conducting polymers.

[0003] Because of its asymmetrical structure, the polymerization of 3-substituted thiophene produces a mixture of PTs structures containing three possible regiochemical linkages between repeat units. The three orientations available when two thiophene rings are joined are the 2,2', 2,5', and 5,5' couplings. When application as a conducting polymer is desired, the 2,2' (or head-to-head) coupling and the 5,5' (or tail-to-tail) coupling, referred to as regiorandom couplings, are considered to be defects in the polymer structure because they cause a sterically driven twist of thiophene rings that disrupt conjugation, produce an amorphous structure, and prevent ideal solid state packing, thus diminishing electronic and photonic properties. A representation of regiorandom couplings is shown in FIG. 2. The steric crowding of the solubilizing groups in the 3 position leads to loss of planarity and less π overlap. In contrast, the 2,5' (or head-to-tail (HT) coupled) regioregular PTs can access a low energy planar conformation, leading to highly conjugated polymers that provide flat, stacking macromolecular structures that can self-assemble, providing efficient interchain and intrachain conductivity pathways. The electronic and photonic properties of the regioregular materials are maximized. A representation of regioregular coupling is shown in FIG. 1.

[0004] Various methods have been employed to synthesize 2,5' regioregular PTs, some of which are described by R. D. McCullough, "The Chemistry of Conducting Polythiophenes", *Advanced Materials*, Vol. 10, No. 2, pages 93-116 (1998), which is incorporated herein by reference in its entirety. The Advanced Materials article describes early and well known methods previously published by R. D. McCullough and R. D. Loewe; (the "McCullough Method") and T. A. Chen and R. D. Rieke (the "Rieke Method"). More recent approaches to regioregular synthesis are described using A. Stille, A. Iraqi and G. W. Barker, *J. Mater. Chem.*, Vol. 8, pages 25-29 (1998), and Suzuki, S. Guillerez and G. Bidan, *G. Synth. Met.*, Vol. 93, pages 123-126, which are incorporated herein by reference. All four methods produce polythiophenes with a high percentage of HT couplings, in the range of 95% or higher.

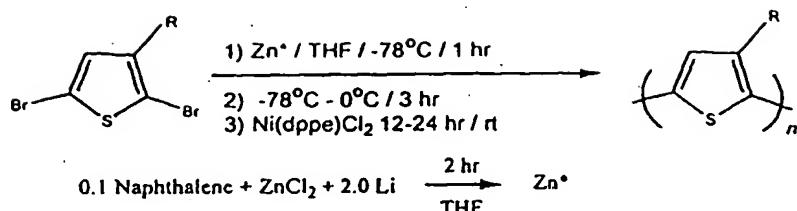
[0005] The McCullough method, developed by one of the applicants of the present invention, synthesizes HT-poly(3-alkylthiophenes) (PATs) at or near about 100% couplings. As illustrated below, this method regiospecifically generates 2-bromo-5-(bromomagnesio)-3-alkylthiophene from a monomer, which is polymerized with catalytic amounts of Ni(dppp)Cl₂ (1,3-diphenylphosphinopropane nickel(II) chloride) using Kumada cross-coupling methods. The McCullough method can be illustrated as follows:

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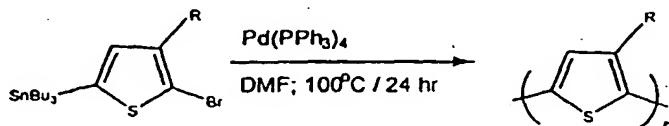


[0006] The Rieke method differs from the McCullough method primarily in the synthesis of the asymmetric organo-metallic intermediate. As illustrated below, a 2,5-dibromo-3-alkylthiophene is added to a solution of highly reactive "Rieke zinc" (Zn⁺) to form a mixture of the isomers, 2-bromo-3-alkyl-5-(bromozincio) thiophene and 2-(bromozincio)-3-alkyl-5-bromothiophene. The addition of Ni(dppe)Cl₂ (1,2-bis(diphenylphosphino)ethane nickel(II) chloride), a nickel cross-coupling catalyst, leads to the formation of a regioregular HT-PATs. The Rieke method can be illustrated as

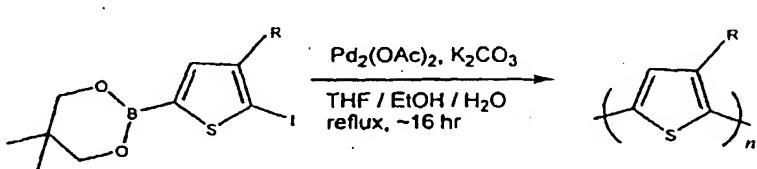
follows:



[0007] Other methods, such as the Stille and Suzuki methods, use a Pd catalyst rather than a Ni catalyst. The Stille method can be illustrated as follows:



[0008] The Suzuki method can be illustrated as follows:



[0009] Despite the efforts by those skilled in the art to improve HT coupling techniques, the synthetic procedures heretofore described have significant drawbacks. For example, the McCullough method requires highly purified starting materials, the most important of which is the monomer, 2-bromo-3-alkylthiophene. The need for purity adds to the cost of the synthesis. The Rieke method includes the easy to purify 2,5-dibromo-3-alkylthiophene as the starting material (because the compound is the highest boiling fraction in the crude mixture in its preparation), but requires the non-trivial preparation of Rieke zinc via alkali metal reduction of zinc halides in an inert environment. The Rieke zinc is very difficult to produce and, therefore, very costly. Both the Stille and Suzuki methods require an extra processing step in their synthesis, thereby decreasing their manufacturing efficiency and flexibility. All of the above illustrated synthesis reactions require cryogenic temperatures at some point during the synthesis, and long polymerization times of 12 to 24 hours or longer. In addition, there have been no reports that any of these known methods have been used for the large scale synthesis of HT-PTs.

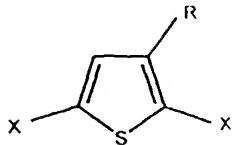
[0010] Accordingly, a new method for the preparation of HT-poly-(3-alkylthiophenes) is needed that is efficient, and economical, provides greater manufacturing flexibility, and is suited for use in large scale industrial processes.

BRIEF SUMMARY OF THE INVENTION

[0011] The present invention solves the above-mentioned problems by providing a new method of forming a polymer. The method includes combining a soluble thiophene having at least two leaving groups with an organomagnesium reagent to form a regiochemical isomer intermediate, and adding thereto an effective amount of Ni(II) catalyst to initiate a polymerization reaction. The reaction yields major amounts of a soluble regioregular polythiophene. The soluble thiophene is preferably a dihalothiophene having a solubilizing substituent thereon.

[0012] The soluble thiophene most preferably is a 2,5 dihalo-substituted thiophene having the structure:

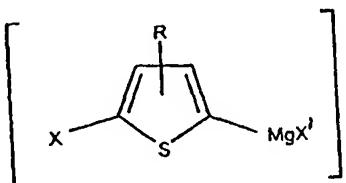
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wherein X may be any halogen, but is preferably Br or I, and R is any non-reactive or protected reactive substituent that is non-reactive with the organomagnesium reagent, such as an alkyl or an ether group.

[0013] The isomer intermediate thus may have the structure:

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[0014] In a preferred embodiment, the present invention provides a method for the large scale preparation of poly-(3-alkylthiophenes) using a 3-substituted thiophene having at least two leaving groups as a starting material. The thiophene starting material is dissolved in a solvent to form a mixture. An organomagnesium reagent is added to the mixture to form a solution. The solution is heated to reflux, and a regiochemical isomer intermediate is formed. A Ni (II) catalyst is added. Following the addition of the catalyst, the solution is stirred at reflux and the reaction is allowed to proceed for a period of time suitable for polymerizing the desired polythiophene product. Thereafter, the product is recovered. If needed, additional reflux time may be provided. The reaction may be quenched prior to recovery of the regioregular poly-(3-alkyl)thiophene.

[0015] The present invention solves problems experienced with the prior art because it offers a method for the production of poly-(substituted)thiophenes that can be carried out in substantially less time at a significantly lower cost than prior art methods. The method of the invention does not require the use of cryogenic temperatures like other prior art methods and preferentially yields relatively major amounts of the desired polymer product, making this method well suited for use on an industrial scale.

[0016] Those and other advantages and benefits of the present invention will become apparent from the description of the preferred embodiments hereinbelow.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

[0017] The characteristics and advantages of the present invention may be better understood by reference to the accompanying drawings, in which:

FIG. 1 is a schematic view of a regioregular polythiophene;

FIG. 2 is a schematic view of a regiorandom polythiophene;

FIG. 3 is a ^1H NMR taken in the aromatic region of HT-poly-3(dodecylthiophene) synthesized using the method of the present invention;

FIG. 4 is a ^1H NMR taken in the methylene region of HT-poly-3(dodecylthiophene) synthesized using the method of the present invention; and

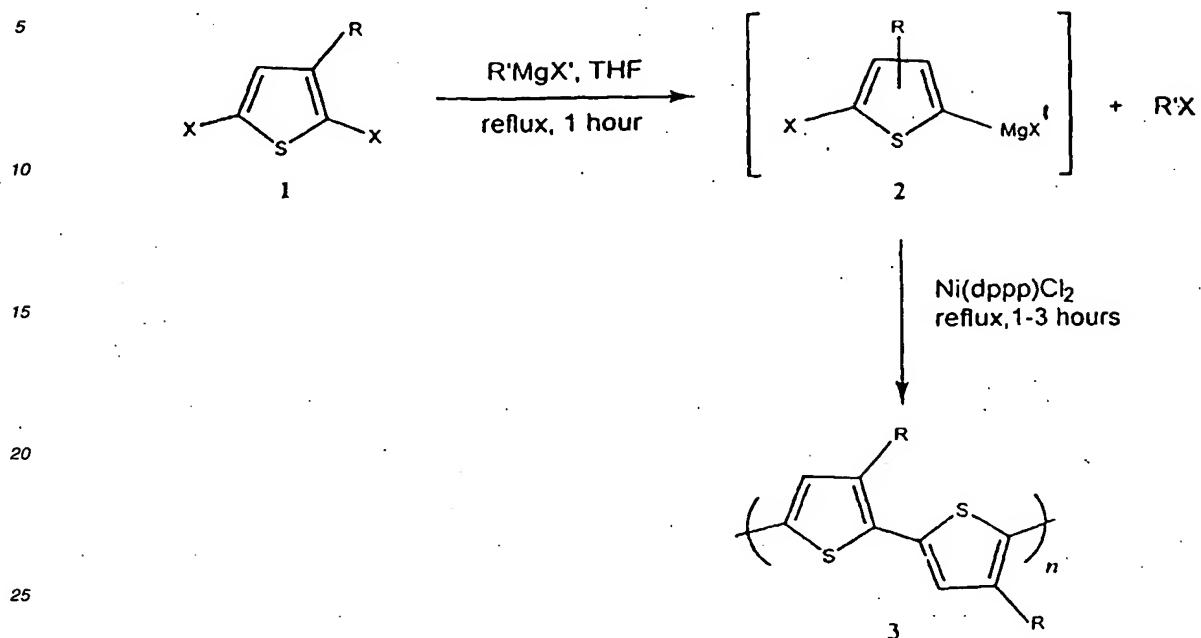
FIG. 5 is a ^{13}C NMR taken in the aromatic region of HT-poly-3(dodecylthiophene) synthesized using the method of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The present invention is a method for producing regioregular polythiophenes. A dihalo thiophene monomer bearing a substituent R to promote solubility is reacted with an organomagnesium reagent in the presence of a solvent for a period of time sufficient to produce a regiochemical mixture of isomers. A polymerization catalyst is added and the reaction proceeds for a period of time sufficient to produce the desired yield of regioregular polythiophenes. The polythiophene product includes major amounts of regioregular thiophene couplings and minor amounts of regiorandom

thiophene couplings.

[0019] The new synthesis for preparing HT-PATs proceeds as follows:



wherein X may be any halogen, such as Br or I, and R may be any non-reactive or protected reactive substituent that is non-reactive with the organomagnesium Grignard reagent ($R'MgX'$). R is preferably an alkyl or an ether group and most preferably an alkyl or substituted alkyl. The organomagnesium reagent ($R'MgX'$) may be any Grignard reagent. X' may be any halogen, but is typically Br or Cl, and R' is typically any alkyl, vinyl, or phenyl group. Examples include, without limitation, $CH_3-CH=CH_2$, $-C_3H_7$, $-C_6H_{13}$, $C_{12}H_{25}$, isopropyl and *tert*-butyl groups.

[0020] The Grignard metathesis reactions are well known in the art, an example of which is described by L. Boymond, M. Rottländer, G. Cahiez, and P. Knochel, *Angew. Chem. Int. Ed., Communications*, 1998, 37, No. 12, pages 1701-1703, which is incorporated herein by reference in its entirety. If R in compound (1) is reactive with the organomagnesium reagent, a protective group should be coupled with the R-group to prevent the R-group from taking part in the synthesis. The use of protective groups with a reactive R-group is well known in the art, as described by Greene and Greene, "Protective Groups in Organic Synthesis," John Wiley and Sons, New York (1981), which is incorporated herein by reference.

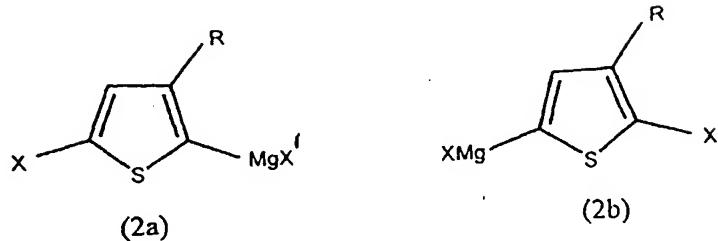
[0021] Compound (1) may be various purified thiophene monomer starting materials, such as a substituted thiophene having two leaving groups, such as a dihalo 3-substituted thiophene. For example, a compound (1) that is greater than 99% pure gives the highest molecular weight yields. Purified, 2,5-dibromo-3-dodecylthiophene is one example, but any halogen and any nonreactive substituent may be used that adds solubility. The leaving groups may be any halogens, such as Br or I. The purified compound (1) may be formed as part of the present process, or may be purchased from a commercially available supplier. For example, when 2,5-dibromo-3-dodecylthiophene is chosen as the starting material, it may be purified, for example, as described in Example 1, below, or it may be purchased from Aldrich Chemical, Milwaukee, Wisconsin. Bromine is preferred over iodine as the leaving group in the starting monomer because the iodine compound substantially increases the toxicity of the reaction. It is believed that chlorine may also be used.

[0022] Compound (1) may be reacted with about one equivalent of an organomagnesium (Grignard) reagent, in refluxing solvent, for a sufficient period of time, about one hour, to produce intermediate regiochemical isomer (2) (as a mixture of regiochemical isomers).

[0023] Any refluxing anhydrous solvent (dry solvent) may be employed in the formation of the intermediate isomer (2), such as tetrahydrofuran (THF). THF is commercially available from Fisher Scientific, Pittsburgh, PA. Formation of the intermediate isomer (2) should be performed at temperatures at or below the boiling point of the refluxing solvent, and can be performed at room temperature (25°C). For example, when THF is employed, the reaction should be performed at its boiling point temperature (66°C).

[0024] The intermediate regiochemical isomer (2) is typically a mixture of regiochemical isomers. For example, it

has been observed that the intermediate isomer (2) may be a combination of:



where (2a) and (2b) are present in either major or minor amounts depending on the choice of R-group. For example, when R is alkyl, the yield for (2a) is about 10-20% and the yield for (2b) is about 80-90%. When R is an ether, particularly a long chain ether, the yield for (2a) is about 60-85% and for (2b) is about 15-40%.

15 [0025] The intermediate isomer (2) may be treated with a Ni(II) catalyst, such as, for example, Ni(dppp)Cl₂ or Ni(dppe)Cl₂ to complete the reaction. When Ni(dppp)Cl₂ is employed, the catalyst may be added in the range of about 0.2-1.0 mol%. The addition of the Ni(II) catalyst may be carried out at temperatures ranging from 0 - 67° C, but is typically performed at room temperature or reflux temperature. The solution may be refluxed for a sufficient period of time, about 45 minutes to three hours or more, to produce the desired polymer. The yield of the CHCl₃ soluble fraction is 60-70% in three hours. The recovered polymer has 95-99% HT-HT couplings, as shown by ¹H NMR. The polymer is also exceptionally pure as shown by elemental analysis.

20 [0026] It is possible to employ the large scale preparation of HT-PTs using the method of the present invention. For example, when 13 grams of 2,5-dibromo-3-dodecylthiophene (1) was polymerized in three hours, 4 grams of pure HT-PDDT was produced. All of the resultant polymers have reasonable molecular weights and low polydispersities, and have about 95-99% HT-HT couplings. For example, when R is dodecyl, M_n = 18-35K, polydispersity index = 1.20-1.67, when R is hexyl, M_n = 13-30K, polydispersity index = 1.13-1.55.

25 [0027] In addition, thiophene monomers bearing polyether side chains can be polymerized by the method of the present invention with somewhat reduced yields.

30 [0028] It is contemplated that the above method may be manipulated so that, for example, shorter reaction times may be employed that produce a lower product yield. For example, as illustrated below in Example 3, when employing 2,5-dibromo-3-dodecylthiophene as the starting material, a 40 minute reaction time yields about 40% HT-PDDT.

35 [0029] As illustrated in FIGS. 1-3, the HT-PDDT yield prepared using the method of the present invention is substantially identical to HT-PDDT yield prepared by other prior art methods, as shown by using ¹H and ¹³C NMR to determine the regioregularity of PATs. FIGS. 3-5 show both the ¹H and ¹³C NMR spectra of HT-PDDT. The high degree of regioregularity can be seen by the appearance of only one singlet in the aromatic region (FIG. 3) as well as a clean triplet in the methylene region of the proton NMR (FIG. 4). As illustrated in FIG. 5, carbon NMR shows only four distinct thiophene carbon resonances. The solid state UV-vis spectra (films cast from 1,1,2,2-tetrachloroethane) of this material is typical of HT-PDDT with a λ_{max} of 569 nm with shoulders at 528 and 620 nm. The band edge occurs at 710 nm.

40 Solution UV-vis (CHCl₃) shows a λ_{max} of 459 nm.

[0030] While the regioselectivity of the metathesis reaction (80:20 mixture of isomers) is high, there is still an even higher degree of regioselectivity displayed in the resulting polymer (99% HT-HT), due to catalyst selectivity. For example, catalyst selectivities of up to 20:1 have also been noted in some couplings of isomers, V. Farina, B. Krishnan, D. R. Marshall, and G. P. Roth, *J. Org. Chem.* Vol 58, No. 20, pages 5434-5444 (1993), which is incorporated herein by reference in its entirety.

45 [0031] The following examples are for illustration only and are not meant to limit the scope of the appended claims.

Example 1

50 [0032] 2,5-dibromo-3-dodecylthiophene (1) was prepared by dissolving 3-dodecylthiophene (19.41 g, 77.06 mmol) in 100 mL of THF. N-Bromosuccinimide (27.43 g, 154 mmol) was added to the solution over a period of 5 minutes. The solution was stirred at room temperature for 2 hours. The solvent was removed *in vacuo* and 250 mL of hexane was added to precipitate substantially all of the succinimide. The mixture was filtered through a plug of silica to remove the added to precipitate substantially all of the succinimide and the solvent was removed *in vacuo*. A Kugelrohr distillation (120°C, 0.02 T) yielded 2,5-dibromo-3-dodecylthiophene (1) (26.26 g, 83.3%) (the highest boiling fraction) as a clear, colorless oil. ¹H NMR (CDCl₃): δ 6.76 (s, 1H), 2.49 (t, 2H), 1.52 (m, 2H), 1.25 (m, 18H), 0.87 (t, 3H). ¹³C NMR (CDCl₃) 143.0, 130.9, 110.3, 107.9, 31.9, 29.7, 29.6, 29.4, 29.1, 25.4, 22.7, 14.1. (Calcd. for C₁₆H₂₆Br₂S: C = 46.84, H = 6.39, Br = 38.95; Found C = 46.51, H = 6.47, Br = 38.69).

[0033] The 2,5-dibromo-3-dodecylthiophene (1.28 g, 3.12 mmol) (1) is dissolved in 18 mL of THF. CH_3MgBr (3.15 mL, 1.0M solution in butyl ether) is added and the mixture was heated to reflux for one hour. The catalyst, $\text{Ni}(\text{dppp})\text{Cl}_2$ (16.9 mg, 1 mol %) was added and the solution was stirred at reflux for 2 hours. The mixture was poured over 150 mL of methanol and filtered into a Soxhlet thimble. Soxhlet extractions were performed with methanol (to remove catalyst, monomer and salts), hexanes (to remove oligomers), and chloroform. The chloroform layer was rotovapped to give a violet film and pumped on for several hours affording 0.510 g (65% yield) of HT-PDDT (3). ^1H NMR (CDCl_3): δ 6.96 (s, 1H), 2.79 (t, 2H), 1.69 (m, 2H), 1.25 (m, 18H), 0.86 (t, 3H). ^{13}C NMR (CDCl_3): δ 139.89, 133.74, 130.52, 128.61, 31.94, 30.56, 29.69, 29.53, 29.38, 22.70, 14.10. (Calcd. for $(\text{C}_{16}\text{H}_{26}\text{S})_n$: C = 76.79%, H = 10.47%; Found C = 76.41%, H = 10.43%).

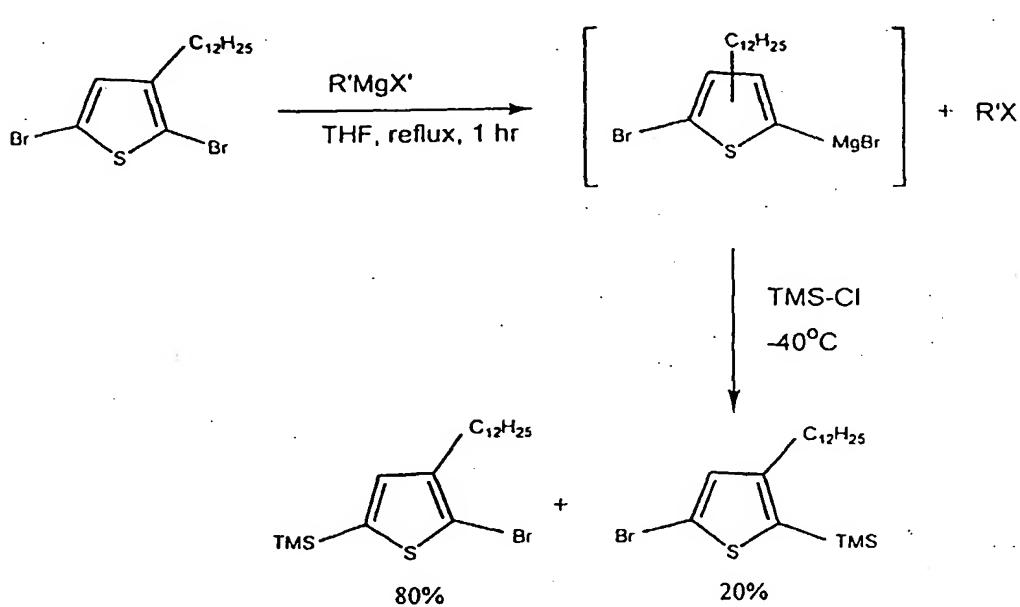
Example 2

[0034] The method of the present invention may be used for the large scale preparation of HT-PDDT (3). The procedure is similar to what has been described in Example 1, above, with 2,5-dibromo-3-dodecylthiophene (1) (13.9 g, 33.8 mmol), 250 mL of THF, and 34 mL of CH_3MgBr (1.0M solution in butyl ether) being refluxed for 50 min, followed by the addition of 196 mg of $\text{Ni}(\text{dppp})\text{Cl}_2$. After refluxing the mixture for another 1 hour and 20 minutes, the reaction was quenched by pouring the reaction mixture into 1.4 L of MeOH. This procedure yielded 40% (3.4 g) of pure HT-PDDT.

Example 3

[0035] The method of the present invention may be used for the short preparation time of HT-PDDT. The procedure is similar to the previous examples described above, with 2,5-dibromo-3-dodecylthiophene (1) (1.8 g, 4.4 mmol), 25 mL of THF, and 4.4 mL of CH_3MgBr (1.0M solution in butyl ether) being refluxed for 20 minutes, followed by the addition of 12 mg of $\text{Ni}(\text{dppp})\text{Cl}_2$. After refluxing the mixture for another 20 minutes, the reaction was quenched by pouring the reaction mixture into 100mL of MeOH. Extraction yielded 40% (420 mg) of pure HT-PDDT.

[0036] The following illustration confirms the presence of a Grignard metathesis. A compound (1) was treated with a variety of Grignard reagents ($\text{R}'\text{MgX}'$) and quenched with trimethylsilyl chloride (TMS-Cl). The reaction is illustrated as:



The quenching results strongly suggests the presence of a magnesium-bromine exchange reaction. Surprisingly, this exchange occurred with a large degree of regiocontrol (80:20 distribution of isomers).

[0037] The regiochemical polymerization method of the present invention provides many advantages over the prior art syntheses. Preparation and purification of the thiophene monomers offer a time-effective method over the prior art, as no more than two reaction steps are required from readily available starting materials. In addition, the corresponding Grignard reagents are cost effective and easy to handle. The method of the present invention does not require the use

of cryogenic temperatures like other prior art methods and has been shown to yield relatively large amounts of the desired product, making this method particularly well suited for industrial scale applications. High yield regioregular, HT-poly-(3-alkylthiophenes) are produced in short reaction times without the need for expensive $MgBr_2$ and $ZnCl_2$ reagents heretofore required. In addition, there is a high degree of regiocontrol displayed in the Grignard metathesis

5 step.
[0038] The regioregular polymers produced by the method of the present invention are useful in a number of commercially important applications. Examples include light emitting diodes (LEDs), field-effect transistors, flat panel displays, smart cards, chemical sensory materials, nonlinear optical materials and microwave absorbing materials for use in stealth technology.

10 [0039] Although the foregoing description has necessarily presented a limited number of embodiments of the invention, those of ordinary skill in the relevant art will appreciate that various changes in the components, details, materials, and process parameters of the examples that have been herein described and illustrated in order to explain the nature of the invention may be made by those skilled in the art, and all such modifications will remain within the principle and scope of the invention as expressed herein in the appended claims. For example, particular detail directed to the use of 2,5-dibromo-3-dodecylthiophene as a starting material has been presented. It should be understood by those skilled in the art that the use of 2,5-dibromo-3-dodecylthiophene in the above examples is illustrative only, and that other starting materials may be employed to yield HT-poly-(3-substituted) thiophenes. All such additional applications of the invention remain within the principle and scope of the invention as embodied in the appended claims.

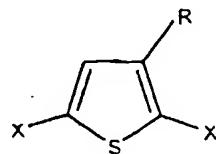
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Claims

1. A method of forming a polymer, comprising:

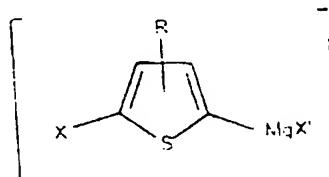
25 combining a soluble thiophene having at least two leaving groups with a haloorganomagnesium reagent to form a regiochemical isomer intermediate; and adding an effective amount of a Ni(II) catalyst to initiate a polymerization reaction.

30 2. The method of claim 1 wherein the soluble thiophene has the structure:



40 wherein R is one of a non-reactive and protected reactive substituent that is non-reactive with the haloorganomagnesium reagent, or X is a Br or I halogen.

45 3. The method of claim 1 wherein the isomer intermediate has the structure:

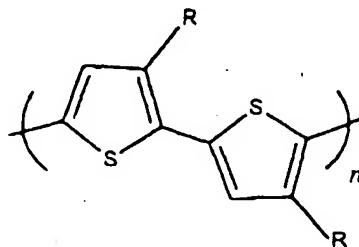


55 wherein R is one of a non-reactive and protected reactive substituent that is non-reactive with the haloorganomagnesium reagent, X is a Br or I halogen, and X' is Cl or Br.

4. The method of claim 2 wherein the haloorganomagnesium reagent has the formula $R'MgX'$, wherein R' is a substituent selected from the group consisting of alkyl, vinyl, and phenyl, and X' is a Cl or Br halogen.

5. The method of claim 1 wherein the Ni(II) catalyst is one of 1,3-diphenylphosphinopropane nickel(II) chloride and 1,2-bis(diphenylphosphino)ethane nickel(II) chloride.

6. The method of claim 5 wherein the Ni(II) catalyst is 1,3-diphenylphosphinopropane nickel(II) chloride and is added to the isomer intermediate to form a polymer having the regioregular structure:



7. A method of forming poly-(3-substituted) thiophene, comprising:

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providing a soluble thiophene having at least two leaving groups; dissolving the soluble thiophene in a solvent to form a mixture; adding a haloorganomagnesium reagent to the mixture; heating the solution to reflux to form a solution containing a regiochemical isomer intermediate; adding a Ni(II) catalyst to the solution; agitating the solution; and recovering the regioregular poly-(3-substituted) thiophene.

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8. The method of claim 7 wherein the solvent is tetrahydrofuran.

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9. An electrically conductive or optically sensitive polymeric material formed from a process, comprising:

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combining a soluble thiophene having at least two leaving groups with an organomagnesium reagent to form a regiochemical isomer intermediate; adding an effective amount of a Ni(II) catalyst to initiate a polymerization reaction; and permitting the reaction to proceed for a period of time sufficient to produce major amounts of regioregular polythiophene.

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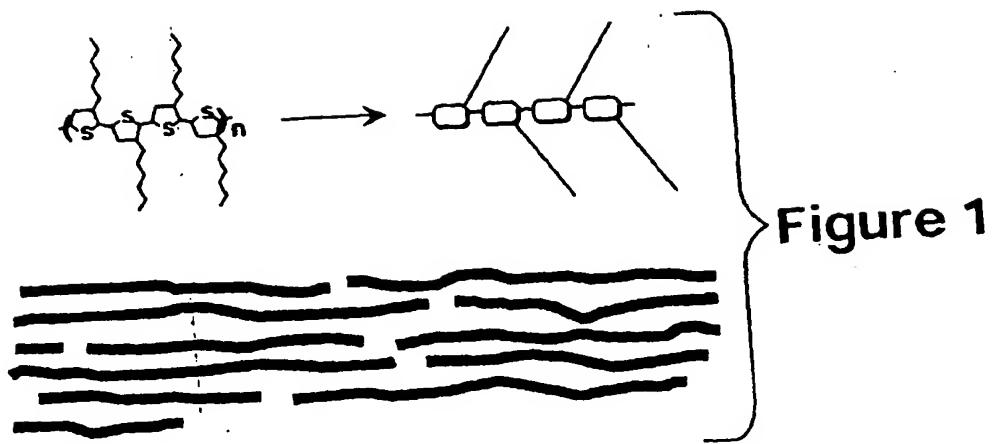


Figure 1

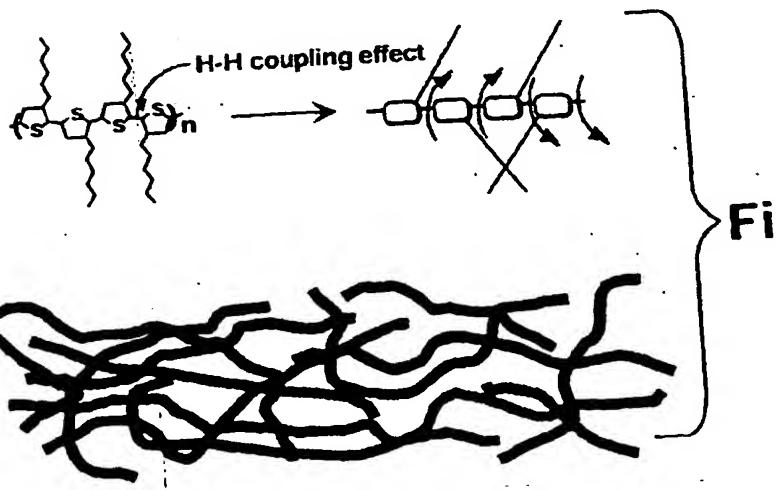


Figure 2

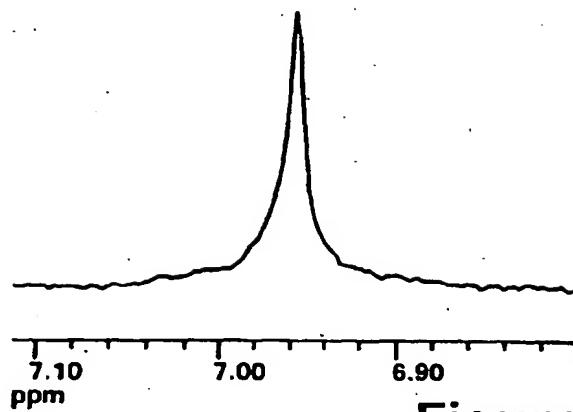


Figure 3

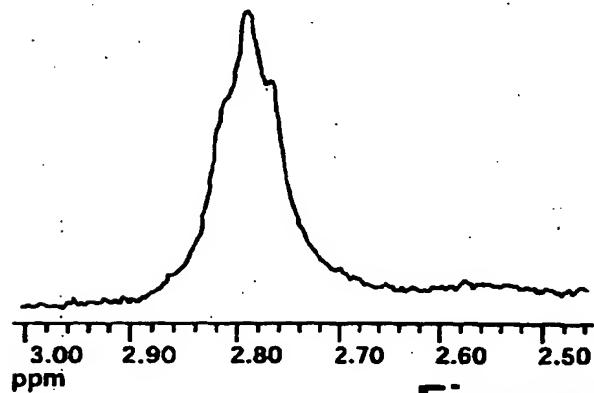


Figure 4

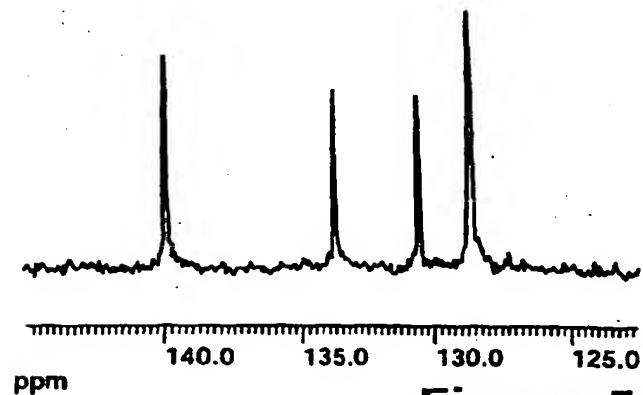


Figure 5

(19)



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(11)

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(54) A method of forming poly-(3-substituted) thiophenes

(57) A method of forming a regioregular polythiophene from a polymerization reaction is described. The method proceeds by combining a soluble thiophene

having at least two leaving groups with an organomagnesium reagent to form a regiochemical isomer intermediate, and adding thereto an effective amount of Ni(II) catalyst to initiate the polymerization reaction.

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EUROPEAN SEARCH REPORT

Application Number
EP 00 10 2714

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X	LOEWE R S ET AL: "A SIMPLE METHOD TO PREPARE HEAD-TO-TAIL COUPLED REGIOREGULAR POLY(3-ALKYLTHIOPHENES) USING GRIGNARD METATHESIS" ADVANCED MATERIALS, VCH VERLAGSGESELLSCHAFT, WEINHEIM, DE, vol. 11, no. 3, 11 February 1999 (1999-02-11), pages 250-253, XP000803285 ISSN: 0935-9648 * page 252 *	1-9	C08G61/12 H01B1/12						
D, X	MCCULLOUGH R D: "THE CHEMISTRY OF CONDUCTING POLYTHIOPHENES" ADVANCED MATERIALS, VCH VERLAGSGESELLSCHAFT, WEINHEIM, DE, vol. 10, no. 2, 22 January 1998 (1998-01-22), pages 93-116, XP000727852 ISSN: 0935-9648 * page 98, column 2 - page 100 *	1-9							
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<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>MUNICH</td> <td>5 September 2001</td> <td>Andriollo, G</td> </tr> </table> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>				Place of search	Date of completion of the search	Examiner	MUNICH	5 September 2001	Andriollo, G
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